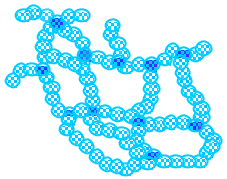
Upstream Environmental Technology Proposal, EP13

Lawrence Livermore National Laboratory and Marathon Oil Company
Joint Proposal

Hydrophobic Membranes for Removal of Organic Impurities in Production Water

John G. Reynolds
Forensic Science Center
LLNL
reynolds3@llnl.gov

Fredrick V. Jones
Marathon Oil Company
fvjones@marathonoil.com



This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

Objective and Goal

- **Objective is to remove contaminant organic compounds from drilling and production waters**
- **Target is oil production platforms**
- **Approach is through hydrophobic aerogel technology**
- **Result is water clean enough to be released into the environment**
- **Goal is to have a process developed ready for commercialization within three years**

Benefits of New Technology

Production water is an environmentally sensitive issue

- **Over 200 million barrels/day of production water**
- **50% is re-injected, 50% discharged**
- **Much discharged water requires treatment**
  - **Metals**
  - **Free oil**
  - **Dissolved organics**
- **Treatment cost ~ $0.6/bbl**
- **Dissolved organics are particularly elusive to treat**

New treatment technology is desirable to lower costs

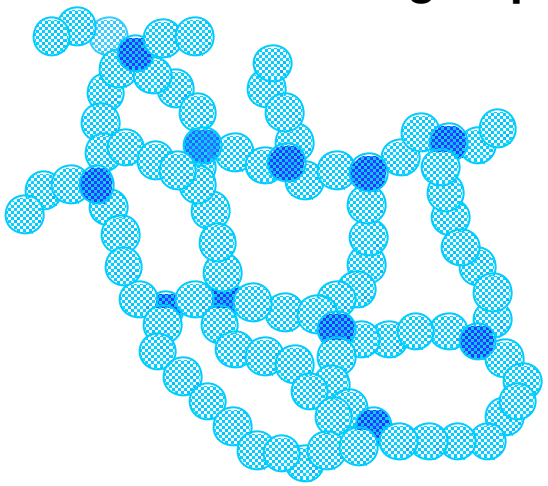
Existing Technologies

- **Free oil**
  - **Centrifuge**
  - **Hydrocyclones**
  - **Membranes**
  - **Coalescers**
- **Dissolved Organics**
  - **Gas stripping**
  - **Biotreatment**
  - **Solvent extraction**
  - **Adsorption**
  - **Oxidation, wet air, UV**
  - **Membranes**

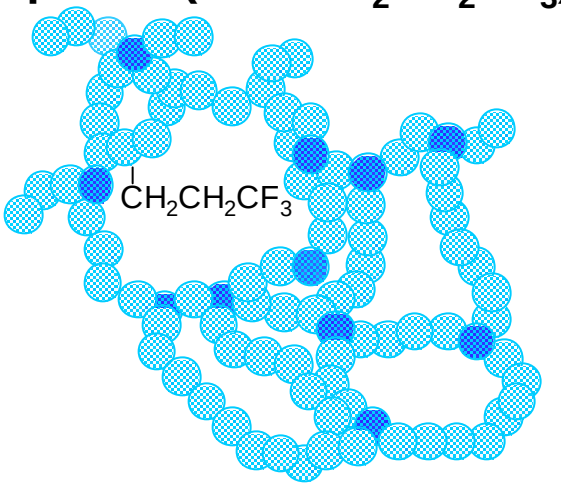
New treatment technology is desirable to better remove dissolved organics

Aerogels are Proposed Materials for Treatment

Unmodified aerogel
Three dimensional string of pearls



Hydrophobic aerogel composite (R = $-CH_2CH_2CF_3$)



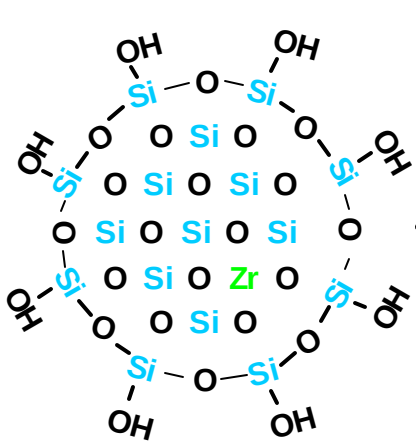
Open foam like structures with high surface areas (100s m^2/g), low densities (0.2 g/cc) and high porosity (90^+%)

Incorporation of R group can vary the chemical properties of the aerogel (hydrophobic)

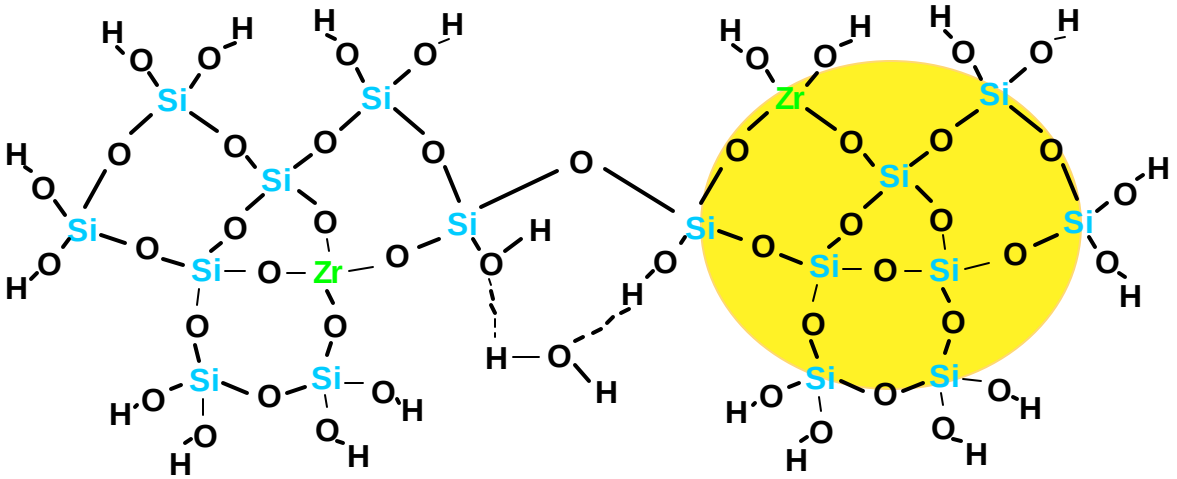
Exceptional properties of chemically modified aerogels may enable an inexpensive means for the large-scale removal of contaminants from aqueous solutions

MARATHON

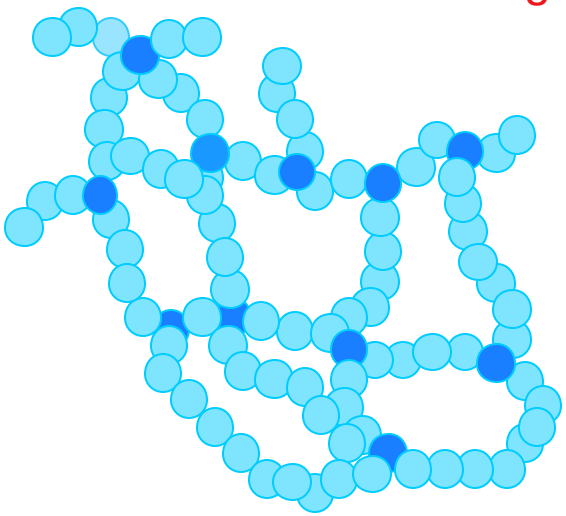
Aerogel Formation Reactions



hydrolysis/
condensation



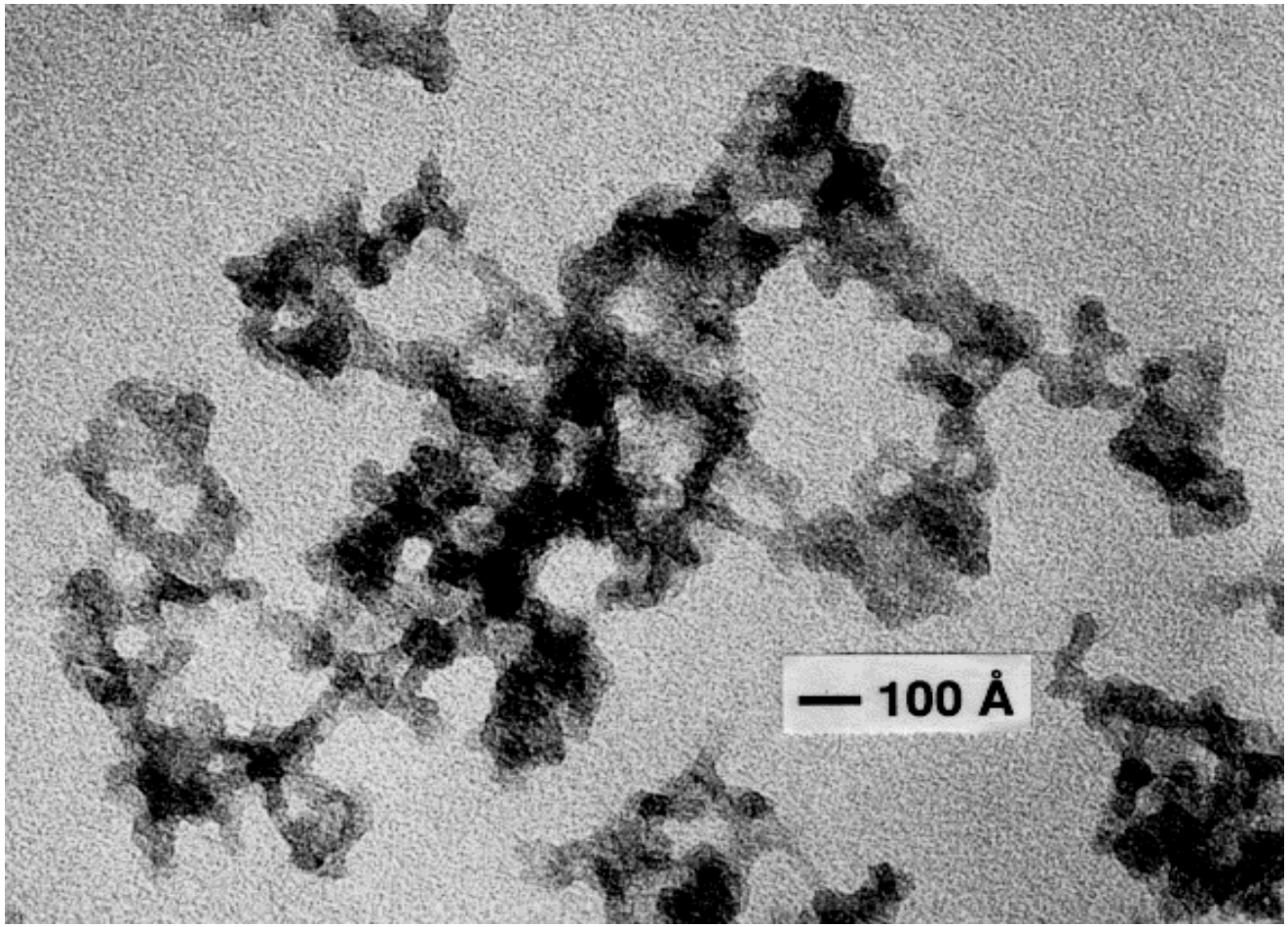
cross-linking



three dimensional array

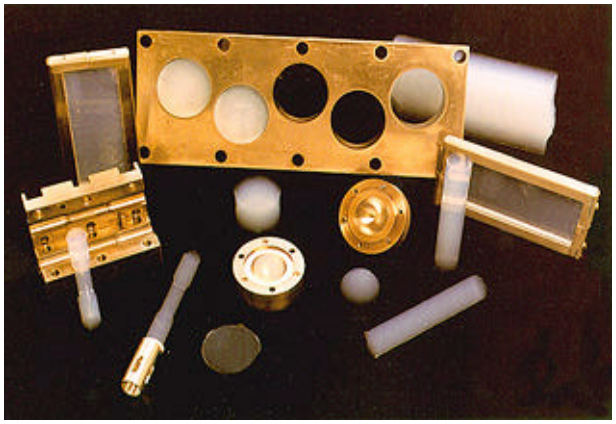
Wet from solvent ⇒ sol-gel
Supercritically dried ⇒ aerogel

TEM of Vanadia-Silica Aerogel



TEM = transmission electron micrograph

Commercial Applications of Aerogels



Aerogels can be cast into many shapes

Materials

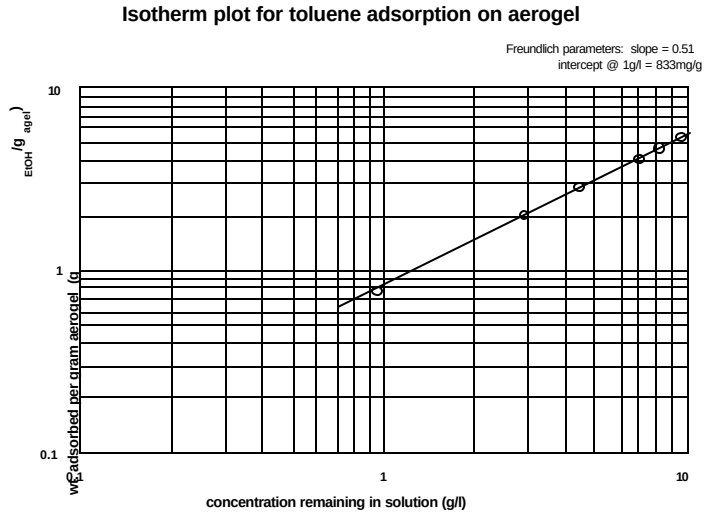
- Thermal and acoustic insulation
- Capacitive de-ionization for water purification
- Light weight lenses and mirrors
- Transparent window insulation
- Energy storage devices
- Chemical detection

First cosmic particle trapped by aerogel

Space exploration

- Insulation for Mars Lander and Sojourner Rover
- Capture medium for cosmic particles on shuttles
- Particle capture on EURECA satellite
- Particle capture on the STARDUST comet mission

Removal of Solvents and Oil from Water



Aerogel out performs carbon in adsorbing organic contaminants from water

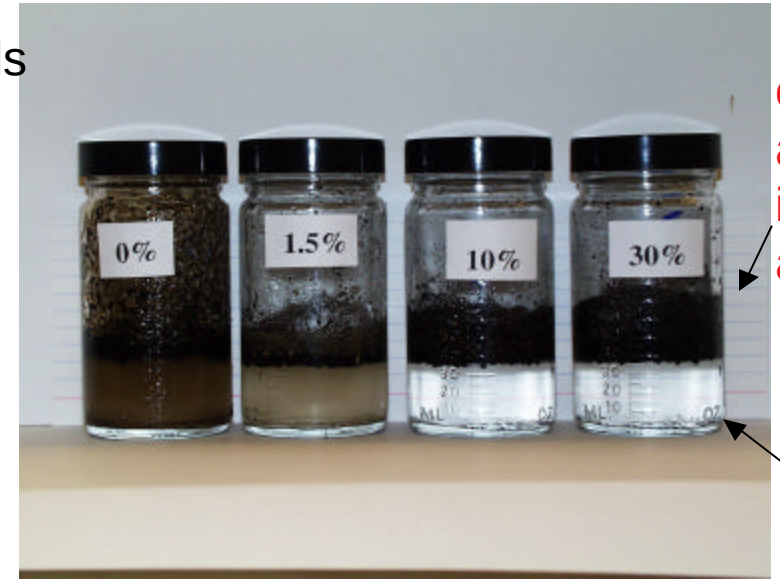
- 32 x better for adsorbing toluene
- 42 x better for adsorbing ethanol
- 131 x better for adsorbing Cl-benzene
- 69 x better for adsorbing TCE

Freundlich isotherm experiment for toluene

Aerogel removes crude oil from oil spills

- adsorbs up to 230 x its own weight
- can be used as a membrane for continuous oil removal
- can be used as coating material for potential cost effective operation

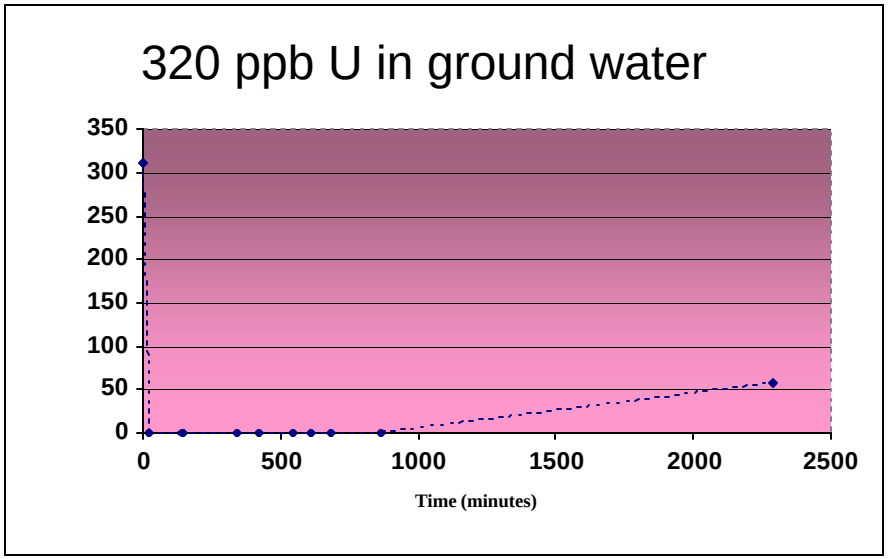
crude oil/salt water mixtures



crude oil adsorbed into aerogel

clear water

Removal of Uranium from Ground Water



Demonstration operation at Site 300

- Site 300 is a remote explosives testing facility for LLNL
- Several areas are contaminated with uranium which is getting in the ground water
- No cost effective method has been approved for the uranium removal
- Modified hydrophobic aerogel/granulated activated carbon composite was tested
- Results indicate complete success

Composite aerogel technology is moving towards commercialization

Technical Approach

- **Use chemically modified aerogels to absorb and separate organics from production water**
  - **Develop modified aerogels to target primarily dissolved organics (hydrophobic)**
  - **Develop optimum deployment method (powder, granular, membrane)**
- **Design integrated process with aerogel for deployment in remote locations (off shore production)**
  - **Pilot plant testing**
  - **Aerogel synthesis scale-up**
  - **Process design**

Aerogels have potential advantages over existing technologies

Technical issues that need to be addressed

- **Adsorption capacity of aerogels for target compounds**
  - Intrinsic kinetics for powdered aerogel
  - Interferences due to ions and salts
  - Effect of form of application
- **Recycle or reuse of aerogel**
  - Regeneration if column use
  - Stability if membrane use
- **Adsorption capacity for real samples**
  - Performance dependant on composition of production water
  - Performance under extreme conditions
- **Scale-up issues**
  - Production of aerogels
  - Pilot plant testing

Deliverables

- 1st year
  - Production methods of aerogels (powdered, granular, and membrane)
  - Intrinsic adsorption kinetics and capacities for powdered aerogels
  - Measurements on surrogate and real production waters
- 2nd year
  - Column testing of granular and composite aerogels (adsorption capacities)
  - Testing of membrane forms of aerogels
  - Selection of form for scale-up
- 3rd year
  - Synthesis of materials for pilot plant testing
  - Pilot plant testing
  - Transfer aerogel synthesis technology to aerogel production company
  - Design full scale treatment facility

Budget

Propose 3 year program
50/50 cost sharing LLNL/Marathon
LLNL contribution from DOE, Marathon contribution in-kind and/or funds in

Year	LLNL	Marathon
First	$300K (1 FTE)	in-kind (1 FTE)
Second	$300K (1 FTE)	in-kind, funds in
Third	$175K (0.5 FTE)	in-kind, funds in

LLNL breakdown - 80% personnel, 20% materials and miscellaneous

Planned activities for Marathon and LLNL

Propose 3 year program
50/50 cost sharing LLNL/Marathon
LLNL contribution from DOE, Marathon contribution in-kind and/or funds in

- **Testing of aerogel for removal of selected organic contaminants representative of typical waste stream**
- **Testing with potential performance inhibitors (scaling compounds, emulsions etc.)**
- **Optimize aerogel composition for best contaminant removal activity**
- **Determine resilience to wear and tear of optimum formulation**
- **Determine optimum method of deployment (single piece membrane, granular, powder, coating) for process**
- **Scale up of aerogel production**
- **Pilot-plant scale-up of process**
- **Full process scale-up**

Laboratory work performed at LLNL
pilot plant and full scale work performed at Marathon